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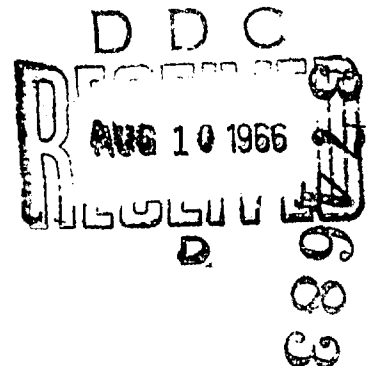| AUTHORITY |
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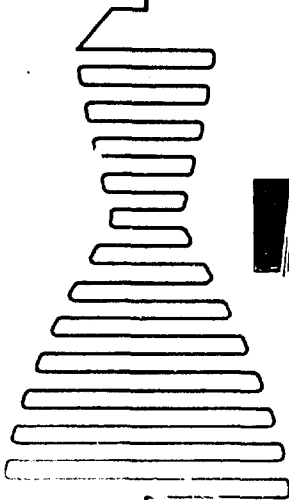
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A DIVISION OF NORTH AMERICAN AVIATION INC
6633 CANOGA AVENUE, CANOGA PARK, CALIFORNIA

R-6641

(Unclassified Title)

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First Assistant Commissioner

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FOREWORD

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ABSTRACT

Oxychlorine trifluoride (ClF_3O) has been synthesized by sev-
eral methods. Excellent yields were obtained by the fluorina-
tion of either Cl_2O or $ClNO_3$, both alone or in the presence of
an alkali metal fluoride. Lesser amounts of ClF_3O resulted
from electric discharge fluorination of solid Cl_2O and the sim-
ple fluorination of $NaClO_2$, and of a mercury salt·Cl_2O complex.

Basic physical properties and analytical data for ClF_3O were
determined. The compound has a boiling point of 29.4 ± 1.0 C
and a melting point of -66 ± 1.0 C with a density of 1.90 ± 0.05
g/cc at 25.5 C. The vapor pressure/temperature equation from
-22 to 32 C is described by $\log_{10} p(mm) = 8.433 - 1680/T$. In
addition, ClF_3O showed good thermal stability in Monel.

Unlike other pentavalent chlorine fluorides, ClF_3O exhibits
marked complexing ability with both acidic and basic fluorides.
Among the latter, complexes with CsF, KF, FNO, and FNO_2 were
investigated. Acid fluorides studied included AsF_5, BF_3,
PF_5, and SiF_4.

On several occasions, pyrolysis of the solids from fluorina-
tion of the CsF·Cl_2O complex yielded traces of an unknown
species (Compound C) which may be FClO. Alternate syntheses
were sought to achieve enhanced yields of Compound C. These
included metathetical displacements on the unpyrolyzed solids
using ClF_3, and fluorination of the CsF·Cl_2O complex under
milder conditions. Thermal degradation and chemical reduction
of ClF_3O were also checked as potential routes to Compound C.

Alkali metal fluorides were found to complex with Cl_2O. These represent a new class of compounds. The most thorough investigation was with CsF where a stoichiometry of $CsF \cdot 1.5 Cl_2O$ was established. Possible bonding schemes are discussed.

The preparation of ClF_5O was attempted by reaction of F_2 with ClF_3O in the presence and absence of CsF and also by reaction of KrF_2 with ClF_3O. No new compounds were observed.

A new procedure was developed for the synthesis of Cl_2O. This method uses simple, static conditions rather than flow conditions. Maximum conversion of the starting materials results according to the equation:
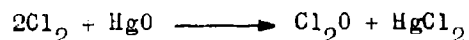
$$2Cl_2 + HgO \longrightarrow Cl_2O + HgCl_2$$

Improved techniques were developed for the formation of $BrNO_3$. Bromine nitrate and Br_2O were employed as precursors in attempts to produce oxybromine fluorides.

The reaction of Cl_2O and AsF_5 was examined and found not to proceed as indicated in the literature. Oxidation and reduction of the Cl_2O occurs giving Cl_2 and probably $ClO_2^+AsF_6^-$.

(Confidential Abstract)

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DISCUSSION

FLOROX* STUDIES

The preliminary characterization of Florox has been completed and entailed
the determination of the chemical composition, some spectral data, several
physical properties, thermal stability and some chemical attributes. In
addition, its synthesis from several starting materials was uncovered.

Preparation of Florox

Synthesis from Cl_2O. Oxychlorine trifluoride was first synthesized by
fluorination of Cl_2O (Ref. 1) both in the presence and absence of added
alkali metal fluoride. The results of additional preparative runs are
presented in Table 1. (A complete description is found in the Experimental
Details of this report.)

TABLE 1

SYNTHESIS OF FLOROX

Alkali Metal Fluoride	Percent Yield	Side Products
CsF	82	$FClO_2$, ClF_3
RbF	≥ 25	$FClO_2$, ClF_3
KF	43, 29	$FClO_2$, ClF_3, ClF
NaF	73, 81	$FClO_2$, ClF
None	39, 63	$FClO_2$, ClF, ClF_3

*Unclassified designation for ClF_3O.

The variation in yields caused by different added alkali metal fluorides is not necessarily significant because of the difference in yields in apparently identical preparations (particularly during CsF experiments where the most data have been gained).

Fluorination of Chlorine Nitrate. After Cl_2O, the best characterized XOCl compound is chlorine nitrate ($ClONO_2$). Preparation of $ClNO_3$ is accomplished by reaction of Cl_2O with either N_2O_4 or N_2O_5 (Ref. 2). Low-temperature fluorinations were conducted on both the cesium fluoride-chlorine nitrate complex and on uncomplexed chlorine nitrate.

On exposure of chlorine nitrate to cesium fluoride at -80 C, a slow lowering of the vapor pressure was observed indicating some complex formation. The reaction was reversible because chlorine nitrate could be removed by warming and pumping. The $CsF-ClNO_3$ complex was treated with excess fluorine at -80 C for several days.

After removal of the excess F_2 at -196 C, the products volatile at ambient temperature were principally FNO_2 and some $FClO_2$ with one case of HNO_3 and N_2O_5 contamination. No further volatiles were evolved even after 4 weeks. Because not all of the starting material was accounted for, the residues were heated to drive off any complexed ClF compounds, in a manner analogous to that used for obtaining pure ClF_3 from $KF \cdot KClF_4$ (Ref. 3). Colorless gases were evolved and these were found to be composed principally of ClF_3O. Much smaller amounts of FNO_2, $FClO_2$, and ClF_3 were also obtained. The yield of ClF_3O based on chlorine nitrate, ranged from 36 to 95- percent except in one reaction wherein previously used CsF was employed and no ClF_3O was found. Complexing of $ClNO_3$ with CsF at -18 C prior to a -80 C fluorination was

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also tried successfully. In high-yield reactions, nitryl fluoride was the only by-product, thus confirming the postulated reaction sequence:

$$ClONO_2 + CsF \xrightarrow{\text{-80 to -18 C}} CsF \cdot ClONO_2$$

$$CsF \cdot ClONO_2 + 2F_2 \xrightarrow{\text{-80 C}} Cs\ ClF_4O + FNO_2$$

$$Cs\ ClF_4O \xrightarrow{\Delta} ClF_3O + CsF$$
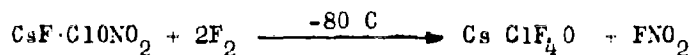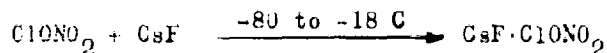
It is also noteworthy that the $ClNO_3$ employed in the highest yield reaction was contaminated with NO_2. The NO_2 impurity had no detrimental effect other than to consume fluorine in being converted to FNO_2.

It was also of interest to utilize chlorine nitrate as an intermediate for the preparation of FClO. Accordingly, a reaction was attempted using uncomplexed $ClNO_3$ and F_2 at -30 C. After several days it was found that Florox was formed in 84-percent yield:

$$ClONO_2 + 2F_2 \longrightarrow ClF_3O + FNO_2$$
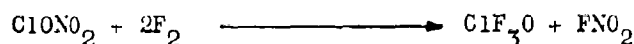
Thus, while no FClO was obtained, it has been demonstrated that the use of CsF is not essential for the formation of ClF_3O and two steps of the previous reaction sequence, complexing and pyrolysis, to liberate ClF_3O, were eliminated. The necessity of alkali metal fluoride catalysis in the Cl_2O fluorination has also been disproved as shown in Table 1. However in both these preparations of ClF_3O, the possible catalytic effect of "bomb fluorides" has not as yet been excluded.

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Fluorination of Mercury Salt·Cl_2O Complex. The synthesis of ClF_3O from Cl_2O generally requires the separation of pure Cl_2O prior to fluorination and in this state Cl_2O has on two occasions exploded. A possible alternate procedure to bypass this step was attempted. The "static" method of preparing Cl_2O indicated the formation of a complex between the Cl_2O and the residual mercury salts. A decrease in the vapor pressure of Cl_2O was observed as well as incomplete Cl_2O removal from the salts at -80 C. Proceeding by broad analogy with the CsF·Cl_2O complex (discussed elsewhere in this report), the preparation of ClF_3O or other new F-Cl-O species was attempted by fluorination.

$$HgCl_2 \cdot Cl_2O + F_2 \longrightarrow ClF_3O + ClF_3$$
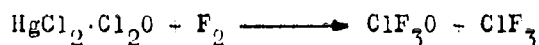
It has been found that this fluorination gives ClF_3O in poor yields. The principal products are ClF_3 and $FClO_2$ with some ClF_5 and occasionally some of the suspected FClO. In addition, the formation of ClF_3O was not reproducible. Early during these experiments it was suspected that moisture originally present in the HgO might have had a deleterious effect on the desired reaction. However, vacuum drying of the HgO before chlorination and fluorination did not change the results other than to eliminate HF as a product.

Electric Discharge Fluorination of Solid Cl_2O. Early during this program (Ref. 1), the use of electric-discharge-activated fluorine was attempted in reactions with solid Cl_2O at -196 C to synthesize ClF_3O. At that time it was observed that some ClF_5 was found but no ClF_3O. This reaction was re-examined using recirculated fluorine in a closed-loop system at low pressures rather than the simple flow through method. As expected, a much more efficient fluorination was achieved. The yield of ClF_5 was approximately 45 percent (based on $2ClF_5$ for each Cl_2O). In addition, small quantities of ClF_3O were found along with some ClF_3 and much $FClO_2$.

Therefore, with the incorporation of this improved technique, the general utility of the electric discharge fluorination process has been improved and made much more efficient. Also, it is expected that this activated gas/solid reaction method might now be employed to demonstrate the synthesis of other highly fluorinated species, in particular ClF_5O.

$$ClF_3O + F_2^* \xrightarrow{\text{-196 C}} ClF_5O$$
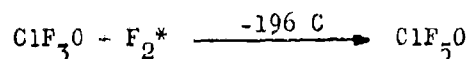
Fluorination of Sodium Chlorite. In an attempt to synthesize oxychlorine fluorides, the static fluorination of sodium chlorite $(NaClO_2)$ has been studied. Although preliminary experiments gave as products small amounts of ClF_3O and Compound C subsequent runs gave neither of these products. Other products from the fluorination are Cl_2, ClF, ClF_3, $FClO_2$, and O_2. Oxygen, Cl_2, and $FClO_2$ are the principal products suggesting the following two reactions:

$$NaClO_2 + F_2 \longrightarrow NaF + FClO_2$$

$$2NaClO_2 + F_2 \longrightarrow 2NaF + Cl_2 + 2 O_2$$
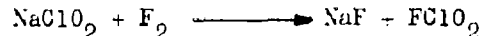
The fluorination is vigorously exothermic both with liquid fluorine at -196 C and with gaseous fluorine at -78 C, accounting for the variety of products and the reduction of chlorite to chlorine despite a strongly oxidizing fluorine atmosphere. Because of the original synthesis of ClF_3O and Compound C by fluorination of $NaClO_2$, the fluorination of potassium perchlorate $(KClO_4)$ have been studied. In both cases, $FClO_2$ and $FClO_3$ were formed instead of the desired products.

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Physical Properties

Preliminary physical characteristics of ClF_3O were reported previously
(Ref. 1). Current data are shown in Table 2.

TABLE 2

PRELIMINARY PROPERTIES OF ClF_3O

Melting Point, C	-66 ±1.0
Boiling Point, C	29.4 ⁓1.0
Molecular Weight	
Found (Vapor Density)	105
Calculated	108.5
Vapor Pressure Equation	$\log_{10}p(mm) = 8.433-1680/T$
Molar Heat of Vaporization, kcal	7.7
Trouton Constant	25.4
Density, g/cc at 25.5 C	1.90 ±0.05

Vapor Pressure/Temperature Relation. The vapor pressure/temperature equa-
tion of oxychlorine trifluoride was determined from -22 to 32 C at nine
temperatures. A least-squares fit yielded the equation $\log_{10} p(mm) =
8.433 - 1680/T$. The normal boiling point of 29.4 C, the heat of vapori-
zation of 7.7 kcal/mole and the high trouton constant indicate a fairly
associated liquid.

Density Measurements. The density of oxychlorine trifluoride was deter-
mined in two ways using a Kel-F pycnometer. A known volume of liquid was
weighed and gave densities of 1.89 and 1.91 g/cc at 25.5 ±1.0 C. The

quantity of gas from a known liquid volume was determined and converted to ClF_3O weight, using 108.5 as the molecular weight. This weight corresponded to a liquid density of 1.95 g cc at 23 C and 2.06 g/cc at 18 C. The direct method not only gave more reproducible data than the gas volume method but allowed calculation of the sample purity by molecular weight as well (105 vs 108.5 theory). Insufficient data were obtained to establish a quantitative dependence of density on temperature.

Thermal Stability of Oxychlorine Trifluoride. Samples of ClF_3O were heated in stainless steel and Monel for periods of 16 hours. Cesium fluoride was added to the stainless-steel cylinders. The runs in Monel were carried out in the presence and absence of fluorine. The data presented in Table 3 show the percent of ClF_3O recovered.

TABLE 3

THERMAL STABILITY OF ClF_3O

| Container	Duration, hours	Temperature, C	Other Material Present	Recovery of ClF_3O percent
Stainless Steel (five runs)	16	200	CsF	0
Monel	16	70	F_2	41
Monel	16	100	F_2	87
Monel	16	200	F_2	63
Monel	16	200	F_2	66
Monel	16	284	F_2	70
Monel	16	290	None	63
Monel	16	200	None	67

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The absence of monotonic results indicates reaction with the container to be more important than thermal degradation. There was no evidence for equilibrium reactions involving ClF_3O.

Elemental Analysis of Oxychlorine Trifluoride

The combustion of ClF_3O and anhydrous ammonia in glass gave nonreproducible results. Metal Teflon reactors were more successful and the following analytical results were obtained: Calculated for ClF_3O: Cl, 32.7 percent; F, 52.5 percent; found: Cl, 30.8 percent; F, 49.5 percent. The low results were attributed to 88- and 94-percent material recovery based on initial ClF_3O gas volumes. The fluorine-to chlorine ratios for the recovered material were 2.97 and 2.99, respectively.

The determination of oxygen in ClF_3O was attempted directly by the reaction:

$$4Hg + 2ClF_3O = HgCl_2 + 3HgF_2 + O_2$$
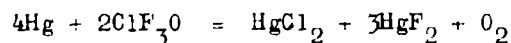
Incomplete oxygen release was observed so an indirect method was tried using sodium chloride:

$$2ClF_3O + 6NaCl = 6NaF + O_2 + 4Cl_2$$
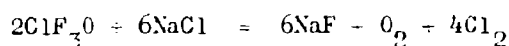
Although the theoretical ratio of chlorine to oxygen was four, ratios from two to eight were obtained by gas/liquid chromatography. More satisfactory results were obtained when NaCl was reacted at 200 C and the oxygen volume was obtained by pumping the oxygen gas at -196 C with a Toepler pump. The following analytical results were obtained: calculated for ClF_3O: O, 14.7 percent; found: O, 12.3 percent.

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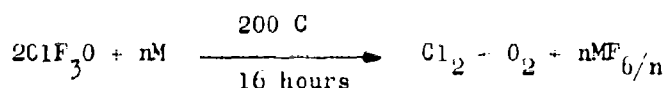
Another method of chlorine and oxygen analysis became available when it was observed that oxychlorine trifluoride reacts with the inside surface of a stainless-steel cylinder at 200 C to give a gas mixture containing only chlorine and oxygen:

$$2ClF_3O + nM \xrightarrow[\text{16 hours}]{200\ C} Cl_2 + O_2 + nMF_{6/n}$$

During four runs, ClF_3O was heated to 200 C in the presence of CsF for a minimum of 16 hours. The condensible gas was measured and compared to the amount of reacted ClF_3O on a molar basis.

The following analytical results were obtained: calculated for Cl_2/ClF_3O: 0.50; found: 0.50, 0.59, 0.48, and 0.49.

The nature of the reaction was confirmed by mass spectrometric analysis of the volatile products of a fifth reaction: Cl_2, 59.9 mole percent; O_2, 40.1 mole percent. The relatively low oxygen content was not unexpected because of the possibility of oxide formation from ClF_3O at 200 C.

In summary, it has been shown that ClF_3O is monomeric in the vapor phase while somewhat associated as a liquid. The molecule has been demonstrated to have a fluorine/chlorine ratio of three and a chlorine/oxygen ratio of one and only one chlorine per molecule. Together these and other physico-chemical data presented herein establish the material as ClF_3O.

Stability of Florox in Hydrogen Fluoride

At least two instances of nonexplosive decomposition of ClF_3O have occurred at Rocketdyne in loading stainless-steel lines which, except for possible HF contamination, were considered passive to ClF_3O. Therefore, the possibility of hydrogen fluoride catalyzed decomposition or reaction with the metal was examined by adding substantially anhydrous HF to ClF_3O in stainless steel and in Kel-F containers. No loss of ClF_3O was observed by infrared analysis in the gas phase, no other compounds being observed besides the ClF_3O and HF even with a tenfold excess of HF at room temperature. Consequently, ClF_3O is stable in HF and the observed decompositions have been attributed to nonpassive line connections.

The Amphoteric Behavior of Oxychlorine Trifluoride

Oxychlorine trifluoride has been found to complex with both acidic fluorides and basic fluorides. It is markedly different in this regard from the other two pentavalent chlorine fluorides, $FClO_2$ and ClF_5, which appear to have little if any affinity for cesium fluoride (Ref. 4 and 5), although workers at Pennsalt (Ref. 5 and 6) report $FClO_2$ and ClF_5 complexes with the less basic fluoride, FNO_2.

Reaction with Fluoride Bases. The acidic behavior of oxychlorine trifluoride has been demonstrated by its complex formation with CsF, KF, FNO, and FNO_2. The ClF_3O-FNO complex has been investigated by low-temperature infrared, n.m.r., and vapor pressure-temperature studies. The ClF_3O-FNO_2 system showed a definite reduction in vapor pressure but has not been studied quantitatively. The evidence obtained from a low-temperature

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infrared investigation of the $FNO-ClF_3O$ solid complex presented in Table 4 supports an essentially covalent structure involving a fluorine bridge.

TABLE 4

INFRARED ABSORPTIONS IN THE $FNO-ClF_3O$ SYSTEM

Sample	Temperature, C	Vibration, cm^{-1}			
		ClF	ClO	NO	NF
ClF_3O	Ambient	674	1225	--	--
FNO	Ambient	--	--	1950	765
ClF_3O-FNO	Ambient	670	1225	1850	765
ClF_3O	-196	685	1250	--	--
FNO	-196	--	--	1990	?
$FNO-ClF_3O$	-196	Broad	1230	2050	?

The ClF_3O-FNO complex was formed by adding a slight excess of FNO to ClF_3O, cycling the mixture between -80 and 0 C, and removing excess FNO by successive expansions at -80 C. A vapor pressure-temperature curve was obtained for the complex from -80 to 0 C: $\log_{10} p(mm) = 8.47 - 1625/T$. From the above equation and the heats of vaporization of the separate liquid constituents a heat of reaction between $FNO(l)$ and $ClF_3O(l)$ was calculated as approximately -5 kcal/mole of complex. This low negative enthalpy of reaction suggested a weak complex in agreement with the infrared data of the solid complex. After the complex was pumped on at -80 C for

1 hour, an infrared examination of its volatile components suggested a 1:2 complex $FNO \cdot 2ClF_3O$. However, prolonged pumping at -80 C resulted in the loss of additional FNO.

The stretching frequencies for NO and ClO in solid FNO and solid ClF_3O, respectively, each increased compared to the frequencies observed in their gas-phase spectra. This suggested that contributions from species such as NO^+F^- were increased slightly. On formation of the solid complex, the ClO frequency was decreased and broadened. These observations suggested a partial transfer of the fluoride of FNO to ClF_3O thus increasing the NO bond order while reducing that of the ClO bond. The N-F band in the solid was either past the instrument range of 15.0 microns or too weak to be observed.

The F^{19} n.m.r. of the $FNO-ClF_3O$ system at 26 C and at -77 C showed only a single broad line 40 ppm downfield from ClF_3O itself. Addition of a fluoride to ClF_3O would be expected to shift the F^{19} resonance to higher fields because of increased shielding in ClF_4O^-. The observed result, while not inconsistent with a contribution from ClF_4O^-, shows that exchange between the NF and ClF fluorines prevents a meaningful interpretation.

Evolution of ClF_3O from CsF-containing solids was achieved by pyrolysis and suggested the presence of the salt $Cs^+ClF_4O^-$. The complex $CsF \cdot ClF_3O$ may be formulated as $Cs^-ClF_4O^-$ by virtue of its relative thermal stability and analogy with other alkali metal fluoride=interhalogen fluoride salts (Ref. 7). This salt represents the first example of a stable pentavalent fluorinated chlorocentro anion. While the formation of the $CsF \cdot ClF_3O$ complex in situ was established during the course of the reaction of $ClNO_3$, it was not known whether it could be prepared directly from ClF_3O and CsF.

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Exposure of ClF_3O to fused and freshly powdered CsF at ambient temperature overnight resulted in almost complete complexing ClF_3O with only small amounts remaining in the gas phase. Pyrolysis of the solids led to evolution of ClF_3O of good purity, demonstrating the reversible reaction:

$$ClF_3O + CsF \xrightleftharpoons[\Delta]{R.T.} Cs^+ClF_4O^-$$

The stoichiometry of the complex was indicated by an experiment using carefully measured amounts of CsF and ClF_3O. With an excess of the latter, an experimental composition $CsF_{1.15} \cdot ClF_3O$ was obtained. This composition is reasonable close to a 1:1 complex, especially considering the problem of solid/liquid contact.

Further studies of the $CsClF_4O$ complex showed that ClF_3O could be displaced from the complex by using another acid. Addition of ClF_3 to $CsClF_4O$ at ambient temperature liberated ClF_3O according to the equation:

$$ClF_3(g) + Cs^+ClF_4O^-(s) \longrightarrow Cs^+ClF_3^-(s) + ClF_3O$$

This confirms ClF_3 to be a stronger Lewis acid than ClF_3O toward CsF.

Reaction With Lewis Acids. The ability of oxychlorine trifluoride to form complexes with acidic fluoride has been demonstrated with AsF_5, BF_3, PF_5, and SiF_4. A nonvolatile equimolar adduct was formed with AsF_5. The BF_3 complex of ClF_3O was formed as a 1:1 complex with ClF_3O which had less than 20 mm Hg dissociation pressure at ambient temperature. The solid dissociated in the gas phase and the spectrum of the gases matched the spectrum of equal amounts of the separate components. The low-temperature infrared spectrum of the

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$ClF_3O \cdot PF_5$ solid complex showed a broad absorption in the PF_6^- region in addition to bands attributed to PF_5. Two strong absorptions at ~1315 cm^{-1} and ~1465 cm^{-1} suggested the existence of ClO_2^+ and ClF_2O^+ arising from $FClO_2$, a known impurity, and ClF_3O, respectively. The ClO absorptions for solid $FClO_2$ and ClF_3O occur at 1280 and 1250 cm^{-1}, respectively and should shift to higher energy with fluoride removal. However, assignments of bands to $ClF_2O^+PF_6^-$ are not possible with the available data. A less stable complex was formed when ClF_3O and SiF_4 were mixed. The vapor pressure of the 2:1 ClF_3O-SiF_4 mixture was measured at several temperatures between -80 and 14 C. The vapor pressure-temperature equation for the complex was obtained: $\log_{10}p(mm) = 7.75 - 1545/T$. The enthalpy change associated with the process $SiF_4(s) - 2ClF_3O(1) = SiF_4 \cdot 2ClF_3O(s)$ was estimated at -2 kcal/mole of complex. Successive portions of the complex were volatilized at -23 C. Their infrared spectra showed a constant ratio of ClF_3O to SiF_4 of 1.9 based on their absorbance ratio. A low-temperature infrared spectrum of the solid complex $SiF_4 \cdot 2ClF_3O$ was identical with the composite spectrum derived from the separate solids within experimental error. Thus, confirmatory infrared evidence on the nature of the complex was not obtained.

POSSIBLE SYNTHESES OF CHLOROSYL FLUORIDE

Pyrolysis of the nonvolatile solid formed by low-temperature fluorination of the Cl_2O-CsF complex has, on at least three occasions, yielded ClF_3O, ClF and traces of an unknown species (Compound C). Compound C is volatile, being only partially trapped at -142 and -160 C in attempted purification by fractional condensation. Two bands in the rock salt region were observed and are indicated in Fig. 1. Additional bands were noted at 645,
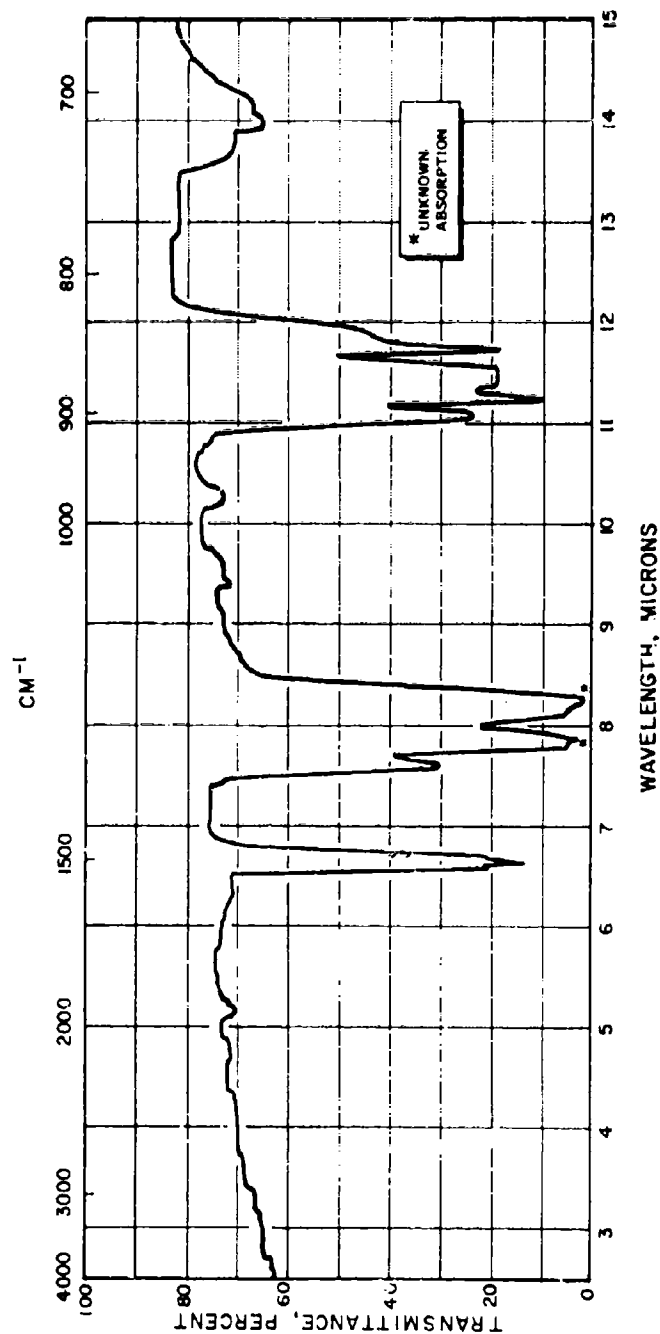
Figure 1. Compound C + SO_2F_2

630, 610 (a possible mqr), and possibly at 465 cm^{-1}. This unknown may be a new F, Cl, O compound and specifically may be FClO. Mass spectrometric examination of a sample containing the unknown yielded no structural information.

Because only traces of the new material were found in the pyrolysis, several new approaches have been utilized in the search for FClO some of which have produced traces of Compound C.

If the material, presumed to be chlorosyl fluoride, were present as a complex such as CsF_2ClO and liberated by pyrolysis, metathetical displacement by ClF_3 might avoid possible thermal decomposition. Three displacement attempts were not successful:

$$[CsF_2ClO] + ClF_3 \xrightarrow{\ ?\ } CsClF_4 + FClO$$
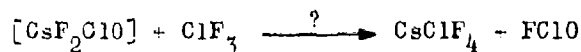
Because the desired FClO may be strongly complexed, even by KF, it was decided to explore the synthesis of FClO from fluorination of Cl_2O both in the presence of NaF and in the absence of any alkali metal fluoride. Instead of producing FClO, however, the low-temperature fluorination of Cl_2O in both cases gave good yields (described elsewhere in this report) of ClF_3O.

The concomitant presence (or absence) of ClF suggested synthesis of the unknown and ClF by a simultaneous degradation of $Cs^+ClF_4O^-$ and $Cs^-ClF_4^-$ complexes. Routine fluorinations of the $Cl_2O \cdot CsF$ complex to ClF_3O and ClF_3 have utilized 3:1 F_2:Cl_2 ratios. Intentional underfluorination to FClO and ClF would require a F_2:Cl_2O ratio of 1:1 according to the equation:

$$CsF \cdot Cl_2O + F_2 \longrightarrow FClO + ClF \cdot CsF$$

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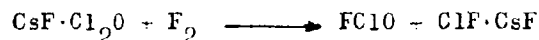
The "incomplete" fluorination at -78 C yielded ClF_3O and much unreacted Cl_2O but only traces of the unknown. Apparently once the $Cl_2O \cdot CsF$ complex was initially attacked by F_2, the chlorine was oxidized all the way to ClF_3O and ClF_3.

Another approach to the synthesis of FClO involves reaction of ClF_3O with appropriate reducing agents. These might include Cl_2O, Cl_2, and ClF. With the reducing agent Cl_2O, FClO could arise as an oxidation product as well as a reduction product:

$$ClF_3O + Cl_2O \longrightarrow 2FClO + ClF$$

A series of reactions between Cl_2O and both ClF_3O and its CsF complex were run in varying reactant ratios at ambient temperature and at -18 C. In all cases the products were ClF and $FClO_2$ in an overall reaction best described by:

$$Cl_2O + CsClF_4O \longrightarrow CsClF_2 + ClF + FClO_2$$
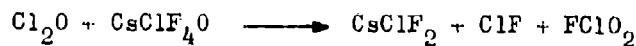
It is possible that the sequence involves formation of the desired FClO followed by its disproportionation:

$$Cl_2O + CsClF_4O \longrightarrow CsClF_2 + [2FClO]$$

$$[2FClO] \longrightarrow FClO_2 + ClF$$
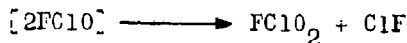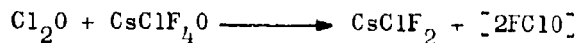
If the intermediate FClO were generated, in no case was it stabilized through complex formation with CsF. With Cl_2 no reaction was observed at ambient temperature with either ClF_3O or its CsF complex. It should be noted that the ClF generated during the Cl_2O experiments also failed to produce FClO by reaction with ClF_3O.

From the initial preparation of Compound C by pyrolysis of a solid complex it was thought that FC10 might result from pyrolysis of ClF_3O as in the following equation:

$$ ClF_3O \xrightarrow{\Delta} FC10 + F_2 $$

Representative results of experiments where Florox at low pressure was passed through a Monel tube held at temperatures from 300 to 585 C are presented in Table 5. As seen in Table 5, decomposition of ClF_3O does not occur to a large extent under these flow conditions at temperatures less than 400 C. Products found at 300 C were ClF_3 and possibly $FC10_2$.

TABLE 5

PYROLYSIS OF ClF_3O

| Temperature	Percent Florox Recovered	Condensible Product Collected at -196 C (as percent of Florox passed)	Products
300	Not Determined	1.5	ClF_3, $FC10_2$
400	99	2	ClF, ClF_3, trace Compound C
450	82	16	ClF
500	46	54	Clf
500	38	62	$FC10_2$, ClF
585	0	98	ClF, trace Compound C

At 400 C, small amounts of ClF as well as ClF_3 were found, and at higher temperatures ClF was the main product. Two reactions yielded traces of the unknown material, Compound C. Material balances agree with the
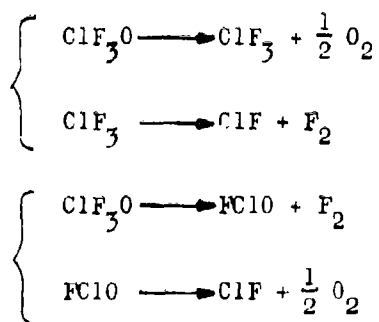
expected evolution of one molecule of ClF (or ClF_3) per molecule of de-composed ClF_3O according to the overall reaction.

$$ClF_3O \longrightarrow ClF + F_2 + \frac{1}{2} O_2$$
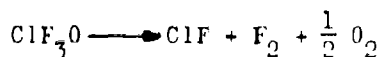
Possible decomposition routes involve either of the following pairs:

$$\begin{cases} ClF_3O \longrightarrow ClF_3 + \frac{1}{2} O_2 \\ ClF_3 \longrightarrow ClF + F_2 \end{cases}$$

$$\begin{cases} ClF_3O \longrightarrow FClO + F_2 \\ FClO \longrightarrow ClF + \frac{1}{2} O_2 \end{cases}$$

No evidence is available to elminate either of these possible routes.

Chlorine fluoride and $FClO_2$ have frequently been found as products in reactions of ClF_3O. The compound FClO may be produced in these reactions as an unstable intermediate, yielding $FClO_2$ and ClF according to:

$$2FClO \longrightarrow ClF + FClO_2$$
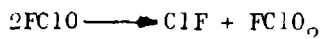
It is possible that the free energy change in this reaction is sufficiently small that increasing the partial pressure of ClF in the proposed equilibrium would result in FClO:

$$2FClO \rightleftharpoons ClF + FClO_2$$
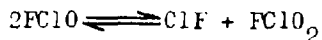
A mixture of interhalogens and interhalogen oxyfluorides collected from many previous experiments and containing large amounts of ClF, ClF_3, and $FClO_2$ was partially separated by fractional condensation. The infrared spectrum of the most volatile fraction revealed the presence of ClF as well as Compound C. Continued fractionation of this volatile sample caused a decrease in the Compound C peaks as $FClO_2$ was removed. Readdition of the $FClO_2$ to the mixture caused an increase in the Compound C peaks.

However, a series of experiments to confirm this proposed equilibrium by reacting ClF with $FClO_2$ was unsuccessful. During one series of experiments, successive additions of FCl to $FClO_2$ failed to show the unknown peaks. Partial pressures of ClF of from 200 to 1000 millimeters were used with a partial pressure of $FClO_2$ of 100 millimeters. Further attempts using large excesses of ClF with $FClO_2$ have not reproduced the unknown peaks at either ambient temperature or 200 C.

Another method to confirm the presence of the elusive FClO would be the preparation of a derivative. If FClO is present even at a very low pressure in equilibrium with ClF and $FClO_2$, addition of F_2 might form the derivative, ClF_3O:

$$ClF + FClO_2 \rightleftharpoons 2FClO$$

$$FClO + F_2 \longrightarrow ClF_3O$$
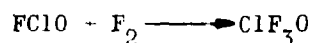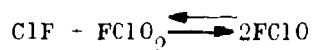
This would both help to confirm the presence of FClO and provide a new route to ClF_3O using only ClF, $FClO_2$, and F_2. A reaction among ClF, $FClO_2$, and F_2 at ambient temperature produced only the expected undesired product ClF_3 while a reaction at −78 C produced no new products.
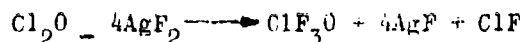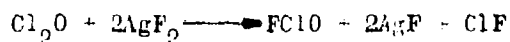
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Reaction of Cl_2O and AgF_2

The fluorination of Cl_2O by AgF_2 has been studied as a possible route to $FClO$ and/or ClF_3O.

$$Cl_2O + 2AgF_2 \longrightarrow FClO + 2AgF + ClF$$

$$Cl_2O + 4AgF_2 \longrightarrow ClF_3O + 4AgF + ClF$$

Silver difluoride was placed in a Monel reaction tube and Cl_2O was passed through it. In the initial reaction with the AgF_2 held at 100 C, the Cl_2O reacted completely producing Cl_2 (main product) and $FClO_2$. Because a subsequent flow experiment at ambient temperature produced the same results, static experiments at -18 and -78 C were conducted. Again only Cl_2 and $FClO_2$ were found. Thus, Cl_2O reacts or is catalytically decomposed by AgF_2 even at temperatures as low as -78 C yielding Cl_2 and O_2 as well as smaller amounts of $FClO_2$.

ALKALI METAL FLUORIDE - Cl_2O COMPLEXES

The alkali metal fluoride complexes of Cl_2O represent a new class of compounds. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide an insight into the paths leading to the formation of oxychlorine fluorides upon fluorination. A brief investigation of the potassium fluoride-chlorine monoxide system and a more thorough investigation of the cesium fluoride-chlorine monoxide system was undertaken to determine the stoichiometry and stability of the complexes. The potassium fluoride complex formed slowly at -78 C and was not stable at -45 C. The formation

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of the $CsF \cdot Cl_2O$ complex occurred in as little as 6 hours at -78 C (as determined by disappearance of Cl_2O color) with excess amounts of CsF. At -23 C, Cl_2O vapor in contact with excess CsF was only one-third complexed after 11 hours. This observation was attributed to enhanced solid/liquid contact at -78 C. To investigate the stoichiometry of the complex formed at -78 C, large excesses of Cl_2O were stored over CsF for several days followed by overnight pumping at -78 C to remove the uncomplexed Cl_2O. Experimental Cl_2O/CsF ratios of 1.52, 0.82, 0.25, 1.5, 1.42, 1.48, and 1.54 were obtained. During another run after the usual overnight pumping to remove excess Cl_2O, an additional 3-1/2 days of pumping removed only 0.17 Cl_2O/CsF. The complex was then warmed to room temperature evolving 1.49 Cl_2O/CsF. The pressure of Cl_2O above such complexes was less than 4 millimeters at -23 C.

It is apparent that a slow forming complex with a Cl_2O/CsF ratio at or near 1.5 is formed at -78 C. A sample of the complexes was exposed to the air, hit with a hammer, and heated with a torch with no explosive results.

The nature of the complexes formed from Cl_2O and CsF are still not understood as to bonding features. Because the most stable complex, as evidenced by relative dissociation temperatures, has an appreciable dissociation pressure at 0 C, it would appear that the bonding involved is rather weak. The bonds may involve an acid-base interaction through fluorine "bridges."

$$F^- \cdot \cdot \cdot ClOCl$$

However, the reproducible stoichiometry of $CsF \cdot 1.5Cl_2O$ may suggest complex structures involving both dative FCl bonds and Cl-Cl bonds. The
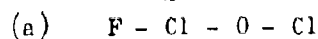
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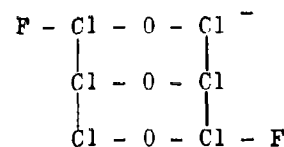**ROCKETDYNE** • A DIVISION OF NORTH AMERICAN AVIATION INC

ClF bonds would arise from the acid-base reaction of F^- and Cl_2O as shown in (a):

(a)   F - Cl - O - Cl

Two anions represented by (a) may be interacting with 1 mole of Cl_2O to give the following resonance structures (all being doubly charged):

$$\begin{array}{c} F - Cl - O - Cl \\ | \\ Cl - O - Cl \quad^- \\ | \\ Cl - O - Cl - F \end{array} \qquad \begin{array}{c} F - Cl - O - Cl \\ | \\ Cl - O - Cl \\ | \\ Cl - O - Cl - F \end{array}$$

$$\begin{array}{c} F - Cl - O - Cl \quad^- \\ | \\ Cl - O - Cl \\ | \\ Cl - O - Cl - F \end{array} \qquad \begin{array}{c} F - Cl - O - Cl \quad^- \\ | \qquad | \\ Cl - O - Cl \\ | \qquad | \\ Cl - O - Cl - F \end{array}$$
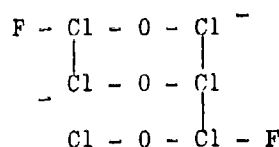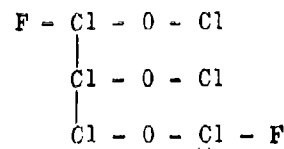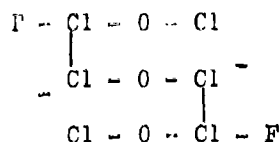
as well as others with the same atomic positions. The hybrid structure may well be a ladder structure such as (b):

$$(b) \qquad \begin{array}{c} \delta^- \qquad \delta^- \\ F - Cl - O - Cl \\ \vdots \qquad \vdots \\ \delta\; Cl - O - Cl\; \delta^- \\ \vdots \qquad \vdots \\ Cl - O - Cl - F \\ \delta^- \qquad \delta^- \end{array}$$
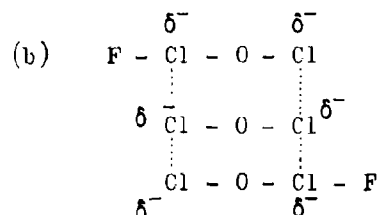
In the absence of the composition $(CsF)_2Cl_2O$ it would not appear that the structure (c) is important despite the higher symmetry. As yet, no
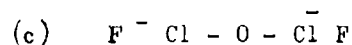
(c)   F ¯ Cl - O - Cl¯ F

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measurements, other than dissociation pressure, have been made on the Cl_2O complexes. The absence of a suitable solvent has made infrared examination of little help thus far. Broad line F^{19} and Cl^{35} spectroscopy may yield qualitative data regarding bond type.

ATTEMPTED SYNTHESIS OF OXYCHLORINE PENTAFLUORIDE

Attempts have been made to react fluorine with ClF_3O to synthesize ClF_5O both in the presence and absence of CsF. In a series of consecutive reactions using only ClF_3O and fluorine in a Monel reactor, five runs from 70 to 284 C yielded no new species. By analogy with the fluorination of $Cs^+ClF_4O^-$ would be expected to provide a more suitable route to ClF_5O.

$$Cs^+ClF_4O^- + F_2 \longrightarrow CsF + ClF_5O$$
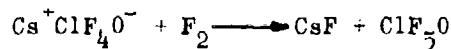
Experiments with increasingly vigorous conditions of temperature and pressure have not resulted in ClF_5O or any other new compound. Conditions used were 750 psi at 50 C, 850 psi at 100 C, and 1200 psi at 160 C for a period of 16 hours or more. The ClF_3O was recovered essentially unchanged from the Monel reactor in each case.

Another possible route to ClF_5O is the direct fluorination of ClF_3O by KrF_2 (Ref. 8) at low temperatures. The possible utility of this reaction is indicated by the recent report of the preparation of ClF_5 from ClF_3 and KrF_2 (Ref. 9).

$$ClF_3 + KrF_2 \longrightarrow ClF_5 + Kr$$

$$ClF_3O + KrF_2 \overset{?}{\longrightarrow} ClF_5O + Kr$$

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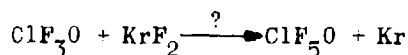
Good mixing of the reactants can only be achieved at temperatures above −65 C, the melting point of ClF_3O. In three reactions, the materials were allowed to warm up together from that temperature to ambient temperature over several hours. No evidence was found, however, for the formation of any new materials. The KrF_2 underwent smooth thermal decomposition to Kr and F_2, and some ClF_3 contaminant was partially converted to ClF_5; the ClF_3O was recovered quantitatively.

A NEW SYNTHESIS OF Cl_2O

Because of the increased requirements for Cl_2O as an intermediate in several preparations essential to this work, an improved synthetic route was desired. The presently accepted, and indeed the only proved method of preparing Cl_2O is via the ambient temperature flow reaction of nitrogen-diluted chlorine and freshly prepared yellow HgO (Ref. 10). This procedure is rather tedious and generally gives 85-percent Cl_2O (15-percent Cl_2) with 60- to 70-percent conversion of the HgO according to the following reported reaction.

$$2HgO + 2Cl_2 \longrightarrow Cl_2O - HgO \cdot HgCl_2$$
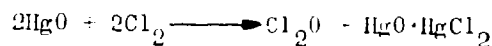
It has been found that the static reaction of HgO and Cl_2 at −80 C, using either the above stoichiometry or excess HgO, produces high-purity Cl_2O in good yield with minimal effort. Furthermore, it has been established that under these conditions at least, the stoichiometry of the reaction approaches:

$$HgO - 2Cl_2 \longrightarrow Cl_2O + HgCl_2$$
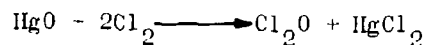
when the Cl_2:HgO ratio exceeds 2:1. The results from some representative preparations are presented in Tables 6 and 7. The Cl_2O yields are for purified material after removal of the Cl_2 impurity.

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TABLE 6

CONVERSION OF Cl_2 TO Cl_2O BASED ON

$$2HgO + 2Cl_2 = Cl_2O + HgO \cdot HgCl_2$$
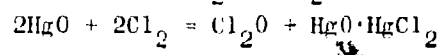
(HgO in excess)

HgO:Cl_2, mole ratio	HgO, millimoles	Cl_2, millimoles	Cl_2O Yield, percent
1:1	9.1	9.06	100
1.08:1	281.6	260.8	79
1.5:1	127.4	84.3	79
2:1	18.2	9.06	77
2:1	18.7	9.33	80
4:1	37.4	9.33	70

TABLE 7

CONVERSION OF HgO TO Cl_2O BASED ON

$$HgO + 2Cl_2 = Cl_2O + HgCl_2$$
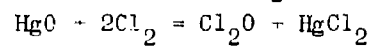
(Cl_2 in excess)

HgO, millimoles	Cl_2O, millimoles	Cl_2O Yield, percent
169	119	70.4
229	129	56.3
277	225	81.2
233	187	80.2
193	184	95.5

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Thus, the technique using excess chlorine gave maximum utilization of the HgO and achieved nearly quantitative conversion of the oxygen of HgO to Cl_2O. Other pertinent advantages of this method were its simplicity and safer handling for gross quantities of the explosive Cl_2O. Because the dispersed Cl_2O was drawn off as required from the mercury salt–Cl_2O reactor, the need to handle large volumes of liquid Cl_2O was eliminated.

The exact mechanism by which Cl_2O is formed from HgO and Cl_2 is not completely understood. It is known, however, that Cl_2O was not all present as free material when in contact with the mercury salts at -80 C. This was demonstrated by the lower vapor pressure (2 millimeters) exhibited under these conditions than that shown by pure Cl_2O (6 to 8 millimeters). Moreover, it was not possible to remove all the Cl_2O by pumping on the mixture at -80 C. Only 50 to 60 percent was evolved at that temperature, the remainder being obtained on warming the reactor to ambient temperature.

X-ray powder analysis of the solid product formed by this reaction using excess Cl_2 showed only lines corresponding to $HgCl_2$. Although the possibility of amorphous or isomorphous mercury compounds exists, apparently the only important reaction under these conditions yields $HgCl_2$.

The possibility of a complex between $HgCl_2$ and Cl_2O was investigated but no reproducible complex formation or reaction was found. The unusual behavior of the solid product observed (i.e., turning brown and evolving small amounts of Cl_2) may be attributed to products formed in amounts too small to be observed by simple X-ray powder analysis.

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FLUORINATION OF Br-0-X COMPOUNDS

The synthesis of oxybromine fluorides was attempted using Br_2O and $BrONO_2$. This work was based on the analogous, proven Cl_2O and $ClONO_2$ reactions which yielded Florox. Fluorination of alkali fluoride complexed Br_2O at -50 C gave as volatile products, BrF_5, unreacted Br_2O, and traces of unstable, unidentified material. While it was anticipated that the sought Br, F, O compounds might remain as complexed solids after the fluorination, pyrolysis up to ~ 400 C did not yield any new products. The failure of this reaction may be caused by the inherent instability of the starting material or thermal degradation of the desired products upon pyrolysis.

Bromine nitrate (Ref. 11) offers two possible advantages over Br_2O as an intermediate in the proposed synthesis of oxybromine fluorides. It is reported to be more stable than Br_2O, decomposing near 0 C vs approximately -40 C for Br_2O (Ref. 12). Also, based on the high yields of Florox obtained by fluorination of uncomplexed $ClONO_2$, the analogous application of $BrONO_2$ can be expected to give similar results while eliminating the necessity of complexing the desirable products.

The synthesis of $BrONO_2$ was conducted according to the reported procedure (Ref. 11).

$$Br_2 + Cl_2 \longrightarrow 2BrCl$$

$$BrCl + ClNO_3 \longrightarrow BrNO_3 + Cl_2$$
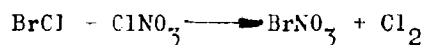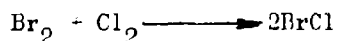
Yields were very low and in fact, usually zero. Because of the sketchy characterization of this material in the literature, no direct evidence for its presence (i.e., infrared spectrum or melting point) was sought

on the small amounts thought to have been formed by this reaction. However, fluorinations yielded no new material and the actual presence of $BrNO_3$ was suspect. Bromine pentafluoride was the only Br-containing material observed.

A new route to $BrNO_3$ was derived which involves the reaction of HNO_3 and BrF_5 or BrF_3. This reaction produced a colorless liquid which decomposed slowly at room temperature. Thus it was possible to obtain an infrared spectrum of the material and observe its vapor-phase decomposition. The reported 0 C decomposition is as follows:

$$2BrONO_2 \longrightarrow Br_2 + O_2 + 2NO_2$$
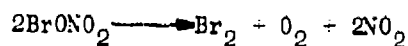
However, this vapor sample was observed to decompose according to the following stoichiometry.

$$2BrONO_2 \longrightarrow Br_2 + 1/2\ O_2 + N_2O_5$$
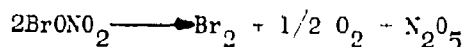
Approximately 50-percent decomposition occurred in 15 hours at ambient temperature. The infrared spectrum of the crude material showed strong absorptions at 5.9, 7.75, and 12.5 microns, representing reasonable shifts from the infrared bands of the analogous FNO_3 and $ClNO_3$ compounds. (The infrared spectrum of $BrNO_3$ has not been reported in the literature.) Fluorination at -80 C resulted in no reaction, the $BrNO_3$ being recovered. This may have been caused by too low a temperature or the inhibiting effect of impurities present (HNO_3, N_2O_5, FNO_2). Reactions at higher temperatures are proceeding with efforts to purify the $BrONO_2$.

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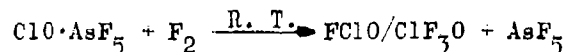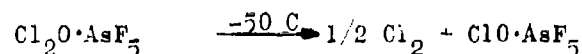REACTION OF AsF_5 AND Cl_2O

As part of the effort to examine various single bonded Cl-O species as possible precursors to oxychlorine fluorides, an investigation of the reported compound, $ClO \cdot AsF_5$ (Ref. 13) was initiated. The reactions reported in the literature, together with the proposed fluorinations, are as follows:

$$Cl_2O + AsF_5 \xrightarrow{-80 \ C} Cl_2O \cdot AsF_5$$

$$Cl_2O \cdot AsF_5 \xrightarrow{-50 \ C} 1/2 \ Cl_2 + ClO \cdot AsF_5$$

$$ClO \cdot AsF_5 + F_2 \xrightarrow{R. \ T.} FClO/ClF_3O + AsF_5$$
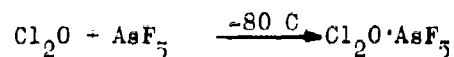
At the outset of this work it was noted that there is a literature discrepancy with regard to the infrared spectrum of AsF_5. Samples of AsF_5 (Ozark-Mahoning) gave an infrared spectrum nearly identical with that reported for "$AsOF_3$", rather than AsF_5 (Ref. 14). But these vendor samples also gave the same infrared spectrum as that obtained for AsF_5 according to the unpublished thesis of L. K. Akers (Ref. 15). To establish the character of the supplied material, a vapor phase molecular weight determination was made. This gave a value of 169.7 gram/mole vs 169.9 for AsF_5 and 147.9 for $AsOF_3$. The mass spectrum of the material showed it to be 90-percent AsF_5 with approximately 10-percent As, O, and F species. Because a vapor-phase chromatogram showed only one component, it appears the sample was pure AsF_5. The As, O, and F impurities undoubtedly arose through reactions of the AsF_5 with an incompletely dry glass inlet system of the mass spectrometer, because HF and SiF_4 were also found in the mass spectrum.

Thus, the infrared spectrum reported by Akers is correct. Mitra's spectrum for "AsOF$_3$" (Ref. 14) consists of AsF$_5$ and the background produced on NaCl infrared cell windows after contact with AsF$_5$. Finally, Mitra's infrared spectrum for AsF$_5$ is identical in all respects with this window background band only (705 cm^{-1}). This was shown experimentally and it is probable that this band is attributable to an AsF$_6^-$ species. For example, K$^+$AsF$_6^-$ salt (Ref. 16) has its strong band at 694 cm^{-1} vs the 705 cm^{-1} observed for this peak.

The reaction of Cl$_2$O and AsF$_5$ when examined at -80 C did not proceed as indicated in the literature (Ref. 13). Mixing the two reactants at -196 C and warming to -80 C resulted in the formation of a dark red solid, which, over a period of several hours became almost black. Pumping on the solid at this point resulted in the evolution of much Cl$_2$ (with little or no -196 C noncondensibles observed).

This Cl$_2$ represents more than half that in the original Cl$_2$O. Further warming to ambient temperature caused additional evolution of small amounts of Cl$_2$ and ClO$_2$. When excess Cl$_2$O was used, no AsF$_5$ was recovered in the volatile phase. Remaining at room temperature was a white solid which exhibited two infrared active bands at 7.9 and 14.6 microns, regions characteristic of Cl=O and As-F absorptions. The solid fumed in moist air and exploded on contact with acid KI. Fluorination of the reaction mixture from which only part of the Cl$_2$ was removed gave the same white solid product on workup. When heated, the solid liberated ClO$_2$ and AsF$_5$. Present evidence, therefore, indicates that the material is probably ClO$_2$·AsF$_5$ or ClO$_2^+$AsF$_6^-$. The latter appears most likely, especially in view of recent findings in somewhat related systems wherein redox of the oxygenated species occurs on reaction with fluorinated complexing agents (Ref. 17 and 18).

$$3N_2O_4 + 8BF_3 \longrightarrow 3NO_2BF_4 + 3NOBF_4 + B_2O_3$$

$$5N_2O_4 + 12\,AsF_5 \longrightarrow 5NO_2BF_4 + 5NOBF_4 + As_2O_5$$
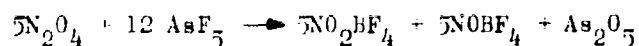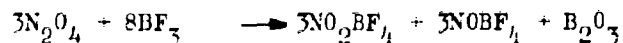
A similar reaction in this system might be:

$$25Cl_2O + 12AsF_5 \longrightarrow 20\,Cl_2 + 10\,ClO_2^{+}AsF_6^{-} + As_2O_5$$
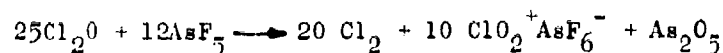
This could account for the high Cl_2 gas values observed, the oxidizing nature of the solid and its simple infrared spectrum and thermal decomposition. The alternate synthesis using $FClO_2$ and AsF_5 will be carried out in an attempt to prove the identity of the solid.

To ascertain the generality of the Cl_2O reaction with Group V fluorides, MF_5 compounds such as PF_5 were examined. It was found that only a weak interaction occurred. The Cl_2O gradually decomposed to ClO_2 and Cl_2, and some of the PF_5 was converted to POF_3. No new materials were obtained.

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EXPERIMENTAL DETAILS

SYNTHESIS OF FLOROX

Fluorination of Cl_2O

Oxychlorine trifluoride, ClF_3O, was synthesized by fluorination of Cl_2O
at -80 C in the presence and absence of added alkali metal fluoride. Suc-
cessful synthetic runs were also carried out at -45, -22, and 0 C. In
most cases the reaction was conducted in a 300-milliliter stainless-steel
cylinder previously passivated by exposure to a minimum of 1 atmosphere
of fluorine for a period of at least 16 hours. Chlorine monoxide and
fluorine were introduced into the reactor by distillation in vacuo and
allowed to react for several days to several weeks. Separation of the
ClF_3O product from side products was achieved in all cases by fractional
condensation. Excess fluorine and any oxygen produced passed -196 C. The
next most volatile side products were $FClO_2$, ClF, and Cl_2 and were removed
by passage through a cold trap at -95 C with the ClF_3O being retained.
Chlorine trifluoride was partially retained at -95 C; therefore, removal
of ClF_3 was achieved by repeated passage through a trap held at -80 C,
with some loss of ClF_3O. In preparations using CsF, RbF, and possibly
KF, pyrolysis of the nonvolatile solid complex yielded additional ClF_3O.

Fluorination of $ClNO_3$

Preparation of Florox from $ClNO_3$ was accomplished in much the same manner
as that using Cl_2O. Complexing where CsF was present, however, could be
conducted at either -80 or -18 C. Work-up of the product was by the
identical procedure stated previously.

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Fluorination of Mercury Salt-Cl_2O Complexes

Yellow HgO and Cl_2 were allowed to react and complex at -80 C for 1 day
or longer. Fluorine was then added at -196 C and the reaction was then
allowed to proceed at -80 C for several days. Vacuum fractionation was
then used to isolate the products which were mostly ClF_3 and $FClO_2$ with
some ClF_5. Oxychlorine trifluoride when found was in low percentage
yields and occasionally also some of the suspected $FClO$ was obtained.

Electric Discharge Fluorination of Cl_2O

Solid Cl_2O was frozen at -196 C near the bottom of a U-shaped discharge
tube. During discharge, F_2 was circulated in a closed-loop system (Ref. 8)
at 20-millimeter pressure until 5 mole/mole of Cl_2O was consumed. Product
work-up was by fractional condensation techniques, as described previously.
The amount of ClF_3O obtained was of the order of 1 to 2 percent.

The ClF_3O used for the vapor pressure-temperature measurements (Table 8)
was purified by repeated fractional condensations. The material was water-
white and free of any impurities detectable by infrared spectroscopy run
at high pressures. Approximately 300 cc of gaseous ClF_3O were utilized
for the measurements which were conducted in a 71-cc volume apparatus.
This was constructed entirely of stainless steel and incorporated a
stainless-steel Bourdon tube pressure gage.

Fluorination of Sodium Chlorite

Three grams of sodium chlorite (Matheson, Coleman, and Bell) were added to
a 300-milliliter stainless-steel bomb. One liter of fluorine was added
by condensation in vacuo at -196 C. The bomb was then allowed to warm to

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TABLE 8

VAPOR PRESSURE-TEMPERATURE DATA FOR ClF_3O

(Equation: $\log_{10} p(mm) = 8.433 - 1680/T$)

Observed Pressure, millimeters	Temperature, K
822	304.9
635	298.1
525	294.3
410	288.6
314	283.0
253	270.9
200	273.2
98	260.6
54.5	250.1

ambient temperature. Products after 66 hours at ambient were ClF_3, Cl_2, ClF, much smaller amounts of Compound C, and possible traces of ClF_3O.

Another run was made by adding an additional 10 grams of $NaClO_2$ to the bomb. Two liters of fluorine was added at -196 C, and the bomb was warmed to -80 C for 16 hours. Volatile products were Cl_2, $FClO_2$, and ClF_3O. Pyrolysis of the solids remaining in the bomb produced no additional materials.

Additional reactions using both gaseous F_2 at ambient temperature and -80 C, and liquid F_2 initially condensed at -196 C and subsequently warmed, produced no additional ClF_3O or Compound C.

PREPARATION OF Cl_2O

Yellow HgO was freshly prepared by the reaction of mercuric chloride and sodium hydroxide solutions. After drying and powdering, HgO was loaded into small glass ampoules together with appropriate amounts of chlorine. The closed, evacuated ampoule was kept at Dry Ice temperature at least overnight, although longer reaction periods were beneficial rather than detrimental to Cl_2O formation. Very pure Cl_2O was obtained if HgO was in excess, while better utilization of the oxygen of HgO was achieved if chlorine was in excess. Impure Cl_2O was upgraded by trap-to-trap distillation using carbon disulfide slush (-112 C) and liquid nitrogen baths. The purity and identity of the product was established by its infrared spectrum (Ref. 19), vapor-phase chromatography and vapor pressure.

With the earlier dynamic method it was necessary to use freshly prepared yellow HgO. However, it was determined that the static method is efficient enough to permit the use of commercial yellow HgO. While the yields

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of Cl_2O are not quite as high as those achieved with the fresh HgO, they are nevertheless quite good; i.e., 90- to 97-percent Cl_2O using either 1:1 or 2:1 HgO to Cl_2 mole ratios. This compares to 95+ percent with fresh HgO. Using the flow technique, the commercial material produces only a 20- to 25-percent conversion of the Cl_2 to Cl_2O. Therefore, if desired, the preparation of fresh HgO may be avoided with only minimal loss of efficiency in the conversion using the static technique.

PREPARATION OF $ClNO_3$

Chlorine nitrate was prepared by allowing roughly equimolar quantities of Cl_2O and N_2O_4 or N_2O_5 to react in evacuated glass ampoules at -80 C overnight or longer. Residual Cl_2O indicated by its red color was consumed by allowing the reaction to proceed briefly in the vacuum line at ambient temperature. The $ClNO_3$ produced was purified by vacuum fractionation and identified by its infrared spectrum (Ref. 20) and vapor pressure (Ref. 21).

LOW-TEMPERATURE INFRARED CELL

The low-temperature infrared experiments were determined in a simple, infrared cell which was constructed as described elsewhere (Ref. 1). The completed assembled cell fits conveniently into a Perkin-Elmer 137 Infracord spectrometer and has a coolant capacity of 2 liters. It can be used at temperatures as low as 77 K and is relatively easy to use with slush baths because the cooling flask is insulated with 3-inch solid foam. The inner window of AgCl fits into a copper optical blank holder. The body is glass and is fitted with two outside AgCl windows.

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Florox complexes were preformed in a metal vacuum line and condensed onto the inner AgCl window at -196 C by means of a copper entrance tube directed at the window.

Dissociation pressure-temperature data for $FNO \cdot ClF_3O$ and $SiF_4 \cdot 2ClF_3O$ are presented in Tables 9 and 10.

TABLE 9

DISSOCIATION PRESSURE-TEMPERATURE DATA FOR $FNO \cdot ClF_3O$

(Equation: $\log_{10} p(mm) - 8.47 - 1625/T$)

Observed Pressure, millimeters	Temperature, K
435	278.6
340	273.2
97	250.1
25	228.1

TABLE 10

DISSOCIATION PRESSURE-TEMPERATURE DATA FOR $SiF_4 \cdot 2ClF_3O$

(Equation: $\log_{10} p(mm) - 7.75 - 1545/T$)

Observed Pressure, millimeters	Temperature, K
340	296.0
158	278.6
170	273.2
40	250.1

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PREPARATION OF KrF_2

Krypton difluoride was prepared by circulating an approximately 1:1 molar mixture of Kr and F_2 through an electric discharge reactor cooled to -196 C. The apparatus and technique are nearly the same as that reported in the literature (Ref. 8). Changing the temperature of the discharge tube to -80 C resulted in no reaction.

PREPARATION OF $BrNO_3$

Bromine nitrate was prepared by allowing excess anhydrous HNO_3 and either BrF_5 or BrF_3 to react in a Teflon container under vacuum at 0 C. Partial purification was achieved through fractional condensations at 0, -45, -80, and -196 C. Pure $BrNO_3$ was not obtained but the presence of the desired material was determined by infrared spectra of crude samples. The decomposition products formed at ambient temperature confirmed the presence of a bromine nitrate species.

REACTION OF Cl_2O and AsF_5

The interaction of these materials was conducted in Teflon-metal containers. A slower reaction with less side products was noted at -80 C, but even at -65 C the basic course of the reaction remained unchanged. For approximately 2:1 mixtures of Cl_2O and AsF_5, the Cl_2 liberated was generally of the order of 80 percent of that contained in the Cl_2O used. Chlorine was identified by its vapor pressure, vapor-phase chromatography, and its lack of infrared absorptions. The small amounts of ClO_2 formed were identified by infrared examination.

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REFERENCES

1. R-6258, Annual Summary Report, Inorganic Halogen Oxidizers, Nonr 4428(00), Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, 30 July 1965, CONFIDENTIAL.

2. Schmeisser, M. and K. Brandle in "Advances in Inorganic Chemistry and Radiochemistry," Vol. V, Academic Press, New York City, 1963.

3. R-5883-2, Inorganic Halogen Oxidizers, Nonr 4428(00), Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, 30 November 1964, CONFIDENTIAL.

4. R-6147, Final Report, Physico-Chemical Characterization of High Energy Storable Propellants, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, 14 May 1965, CONFIDENTIAL.

5. PCC-8518-QR-12, Synthesis of Inorganic Oxidizers, Pennsalt Chemical Corp., King of Prussia, Pennsylvania, 1 March 1966, CONFIDENTIAL.

6. PCC-8518-QR-8, Synthesis of Inorganic Oxidizers, Pennsalt Chemical Corp., King of Prussia, Pennsylvania, 1 March 1965, CONFIDENTIAL.

7. Whitney, E. D. et al.: J. Am. Chem. Soc., 86, 2583 (1964).

8. Schreiner, F. et al: J. Am. Chem. Soc., 87, 25 (1965).

9. Malm, J. G.: Presented at the International Symposium on Fluorine Chemistry, Munich, Germany, September 1965.

10. Cady, G. H. in "Inorganic Synthesis," Vol. V, McGraw Hill, New York, 1957, p 156.

11. Schmeisser, M. and L. Taglinger, Chem. Ber., 94, 1533 (1961).

12. Schwarz, R. and H. Wiele: J. prakt. Chem., 152, 157 (1939).

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13 ABSTRACT Oxychlorine trifluoride (ClF_3O) has been synthesized in excellent yields by the fluorination of either Cl_2O or $ClNO_3$. Lesser amounts of ClF_3O resulted from electric discharge fluorination of solid Cl_2O and the simple fluorination of $NaClO_2$, and of a mercury salt Cl_2O complex. Basic physical properties and analytical data for ClF_3O were determined. The compound has a boiling point of 29.4 ± 1.0 C and a melting point of -66 ± 1.0 C with a density of 1.90 ± 0.05 g/cc at 25.5 C. The vapor pressure/temperature equation from -22 to 32 C is described by $\log_{10}P(mm) = 8.435 - 1680/T$. In addition, ClF_3O showed good thermal stability in Monel. On several occasions, pyrolysis of the solids from fluorination of the $CsF \cdot Cl_2O$ complex yielded traces of an unknown species (Compound C) which may be $FClO$. Alternate syntheses were sought to achieve enhanced yields of Compound C. Alkali metal fluorides were found to complex with Cl_2O. These represent a new class of compounds. The most thorough investigation was with CsF where a stoichiometry of $CsF \cdot 1.5Cl_2O$ was established. Possible bonding schemes are discussed. The preparation of ClF_5O was attempted by reaction of F_2 with ClF_3O in the presence and absence of CsF and also by reaction of KrF_2 with ClF_3O. An improved procedure was developed for the synthesis of Cl_2O. Maximum conversion of the starting materials results according to the equation: $2Cl_2 + HgO \rightarrow Cl_2O + HgCl_2$. Improved techniques were developed for the formation of $BrNO_3$. Bromine nitrate and Br_2O were employed as precursors in attempts to produce oxybromine fluorides. The reaction of Cl_2O and AsF_5 was examined and found not to proceed as indicated in the literature. Oxidation and reduction of the Cl_2O occurs giving Cl_2 and probably $ClO_2^+ AsF_6^-$. (C)

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